

Hydrogen and syngas production from gasification of lignocellulosic biomass in supercritical water media

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Abstract

Purpose Novel biomass-processing technologies have been recently used for conversion of organic wastes into valuable biofuels like bio-hydrogen. Agricultural wastes are available and renewable energy resources to supply energy demand of the future. The purpose of this study is to investigate the production of hydrogen-rich syngas from wheat straw, walnut shell, and almond shell.

Methods Supercritical water gasification is a promising technology to convert biomass into useful fuels. Non-catalytic conversion of wheat straw, walnut shell, and almond shell into the hydrogen-rich gas in supercritical water media was performed using homemade batch microreactor system.

Results Hydrogen gas yields of 6.52, 4.26 and 4.1 mmol per 1 gram of wheat straw, walnut shell, and almond shell were observed, respectively. In addition, hydrogen and carbon gasification efficiencies equal to 42.6 and 46.9 % were calculated from gaseous products and elemental analysis of wheat straw, which were higher than other feedstocks' gasification efficiencies.

Conclusion Wheat straw had the highest and walnut shell had the lowest total gas and hydrogen gas yields. Taking into account the structural analysis, it was recognized that feedstocks with higher cellulose and hemicellulose and lower lignin contents were better gasified due to their easier hydrolysis and higher solubility in water.

Keywords Biomass · Hydrogen production · Gasification · Supercritical water media

Introduction

Sustainable development in the context of energy is one of the most important road maps for scientists and engineers in recent years. Using renewable energy resources, maximizing energy efficiency and improving energy conservation with novel methods are the strategies for achieving this aim. Research and development in methods of obtaining power from energy resources with less environmental effects and higher efficiencies would be a great leap forward in this way. Biomass is an available and renewable resource that easily can be obtained from nature. Wasting this resource results in harmful environmental effects and causes many problems, while it can be converted into useful products such as hydrogen by different conversional technologies. Conversion of biomass into these products is helping us to supply the energy demand of the future in a sustainable way. Many scientists regard hydrogen as a key energy carrier of the future. The amount of energy released during hydrogen combustion is higher than any other fossil fuels on a mass basis, with a lower heating value (LHV) 2.4, 2.8 and 4 times higher than that of methane, gasoline and coal, respectively. Generally, we have two main methods for hydrogen production from biomass. Thermochemical method, which is divided into three types of processes (pyrolysis, gasification and SCWG) and biological methods (Hepbasli et al. 2009).

In this study, we perform supercritical water gasification that is one of the most promising methods for thermochemical conversion of biomass into hydrogen-rich gas. This technology has many advantages compared with other

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thermochemical conversions. In this method, wet biomass can be converted into the hydrogen-rich syngas at lower temperatures with higher efficiencies due to the high dispersion and effective heat transfer of water in its supercritical condition (374 °C, 22.1 MPa) (Saxena 2008). Water in SCWG has a twofold role as reaction medium and reactant. The unique solvent properties allow supercritical water to solve the major part of biomass and reform it through a homogeneous mixture. Water–gas shift (producing H_2 and CO_2 from CO and H_2O) and methanation (producing CH_4 and H_2O from CO and H_2) reactions occur with biomass reforming in supercritical water, simultaneously (Calzavara et al. 2005).

Modell et al. (1978) reported the effect of temperature and concentration on the gasification of glucose and maple sawdust in water in the vicinity of its critical state. No solid residue or char was produced. Hydrogen gaseous yield up to 18 % was observed. After that, research and development on this method increased significantly. Guo et al. (2007), concluded that carbohydrates (i.e. cellulose and hemicelluloses) gasified much easier than xylen and lignin, and lignin was the most difficult to gasify. In addition, it was realized that lignin can interact with cellulose and change both the gas yield and product gas composition. Other researchers expressed that, in SCW gasification of real biomass feedstock, char/coke may originate from non-decomposed biomass by a solid–solid conversion; and coke formation in biomass gasification process due to the presence of lignin, not only depends on the lignin amount but also strongly depends on the structure of lignin and interactions between other components in the real biomass (Yanik et al. 2007). In the recent years, Tavasoli et al. (Barati et al. 2014) have studied the gasification of sugarcane bagasse in supercritical water condition. Hydrogen yield up to 37 % was observed in tubular batch microreactor, which was for the gasification in the temperature of 400 °C, with biomass loading of 0.05 g and water loading of 4 g in reaction time of 15 min. It was also shown that hydrogen yield was increased with the increment of reactor's temperature while it was decreased with the increment of feed concentration.

In this article, we investigate the gasification of wheat straw, walnut shell and almond shell in supercritical water media with tubular batch reactor, which is designed for the efficient reacting condition, considering the latest experiments and research literature.

Materials and methods

Materials

The biomass particles used for the experiments were obtained from gardens and agriculture farms around

Sanandaj, located in Kurdistan province, Iran. They were dried under atmospheric conditions for 48 h, and ground to particle sizes <150 micrometer in diameter. The elemental compositions of the whole biomass samples were analyzed in a CHNS analyzer.

Reaction setup and experimental outline

A batch microreactor made of 316 stainless steel tube with total volume of 23 mL has been used in this study (Fig. 1a). Variation of the reactor's pressure with time is shown in Fig. 1b. Feedstocks were mixed with a certain amount of deionized water and injected into the reactor using a syringe. The reactor was plunged in a molten salt bath that contained a mixture of potassium nitrate, sodium nitrate, and sodium nitrite. The molten salt bath temperature was controlled using an electrical heater and a PID temperature controller. Temperature and pressure were measured using a K-type thermocouple and a pressure gauge. Figure 1b, shows the typical changes in reactor pressure. After a given reaction

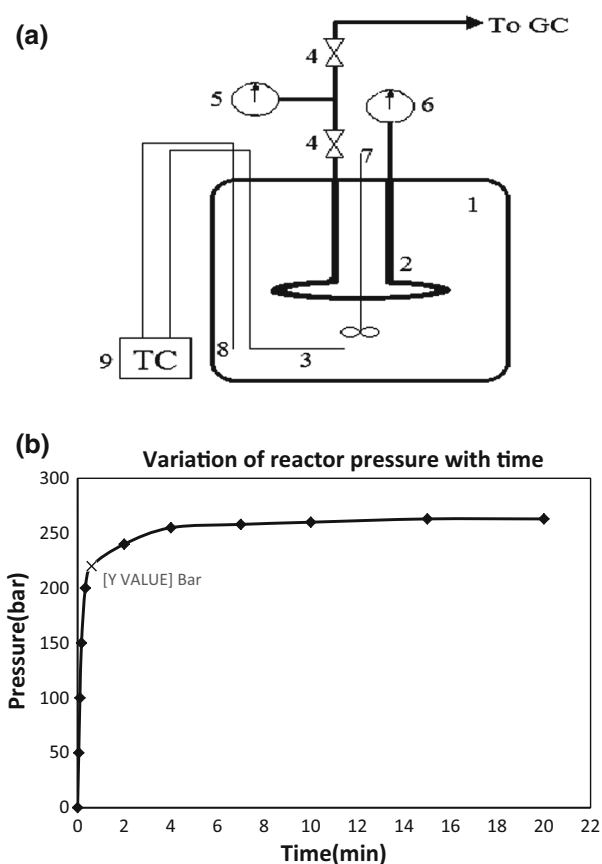


Fig. 1 **a** Scheme of the homemade tube batch microreactor: 1 molten salt bath 2 batch tube reactor, 3 electrical heater, 4 high-pressure valve, 5 low-pressure gauge 6 high-pressure gauge, 7 mixer 8 k-type thermocouple, 9 temperature controller. **b** A typical variation of reactor's pressure with time (T 440 °C, wheat L 0.05 g, water L 5 g)

time, the reactor was taken out of the molten salt bath and plunged in a water bath for rapid cooling to room temperature. All experiments were performed three times and the data reported here are the averages of repetitive runs.

At the end of each experiment, reactor free volume, final pressure and temperature were used to calculate the gas yield. The amounts of each product's gases were measured and analyzed using gas chromatographs (Varian 3400 and Teyfgostar-Compact). The carbon gasification efficiency (CGE), which is the ratio of the amount of carbon in the gaseous products to the amount of carbon in the biomass; and hydrogen gasification efficiency (HGE), which is the ratio of the amount of hydrogen in the gas phase to the amount of hydrogen in the biomass were measured after each experiment. Mathematically, CGE and HGE are defined as (Barati et al. 2014):

$$\text{CGE} = \frac{\{Y_{\text{CO}} + Y_{\text{CH}_4} + Y_{\text{CO}_2} + 2Y_{\text{C}_2\text{H}_4} + 2Y_{\text{C}_2\text{H}_6}\}}{\{\text{mmol Carbon/g biomass}\}} \quad (1)$$

$$\text{HGE} = \frac{\{Y_{\text{H}_2} + 2Y_{\text{CH}_4} + 2Y_{\text{C}_2\text{H}_4} + 3Y_{\text{C}_2\text{H}_6}\}}{\{\text{mmol H}_2/\text{g biomass}\}} \quad (2)$$

Results and discussion

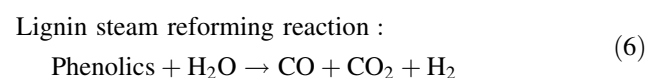
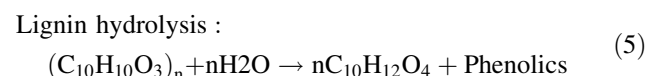
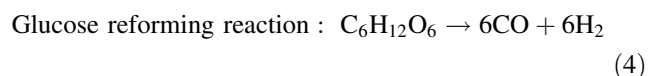
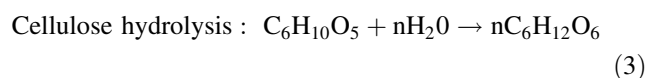
Feedstock analysis

The feedstocks used in this study are lingo-cellulosic biomass. A lingo-cellulosic biomass typically has 30–60 % cellulose, 20–40 % hemicellulose and 15–25 % lignin (Nanda et al. 2013). The CHNS and structural analyses of the biomasses are given in Table 1. As indicated, the C and H content in the samples are 48.25 and 6.08 % for wheat straw, 50.2 and 5.67 % for walnut shell, and 49.70 and 5.43 % for almond shell, respectively. The balances are mostly oxygen. In addition, structural analysis shows that the lignin contents in their structure are 19.3, 35 and 38 %, respectively, for wheat straw, walnut shell and almond shell.

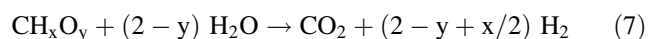
Reactions

Because of the lingo-cellulosic structure of biomasses used in this study, it is necessary to study the behavior of the

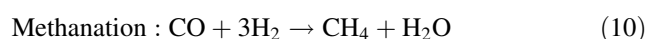
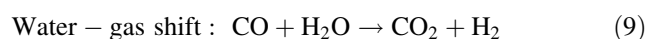
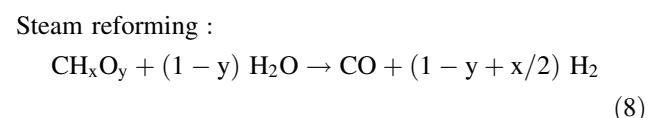
intermediates and their degradation or reformation routes to gases. Prior to understanding the mechanisms, behavior and the breakdown of the complex lingo-cellulosic biomass in supercritical conditions, it is essential to investigate the SCWG of their model compounds such as cellulose, glucose, glycerol, lignin and phenolics. Some of the vital reactions that occur during the gasification of biomass in SCW are as given below (Reddy et al. 2014).



Supercritical water gasification of biomass is a complex process but the overall conversion can be simplified as:



Thus x and y are the elemental molar ratios of H/C and O/C in biomass composition. This is an endothermic reaction and shows the reactance effect of water in addition to its solubility, and hydrogen in the water is released by the gasification reaction. In addition to reaction (7) some intermediate reaction can occur in order to complete the gasification process that is mentioned as follows (Rashidi and Tavasoli 2014; Ataei and Azimi 2012).



The reforming reactions produce CO, CO₂ and H₂, whereas CH₄ is produced by methanation and hydrogenation reactions. Water–gas shift reaction (WGS) is another significant reaction of SCWG of biomass. It is obvious that water–gas shift should be accelerated and methanation should be avoided when hydrogen-rich gas is required (Reddy et al. 2014).

Table 1 Elemental and structural analysis of different feedstocks

Feedstock	Element analysis (CHNS) (%wt)					Structural analysis (%wt)		
	S	N	H	C	O	Lignin	Cellulose	Hemicellulose
Wheat straw	0.22	2.11	6.08	48.25	42.80	19.30	39.80	27.30
Walnut shell	0	0.84	5.67	50.2	42.64	38	36	25.43
Almond shell	0.06	1.10	5.43	49.70	41.60	35	30.70	32.60



Product analysis

Total gas yield and its composition is presented in Fig. 2, for the determined condition. The carbon and hydrogen gasification efficiency was also calculated and presented in Fig. 3. As shown, wheat straw has the highest hydrogen yield with 6.52 mol/g. Moreover, wheat straw has the highest hydrogen and carbon gasification efficiencies equal to 42.6 and 46.9 %, respectively. The total gas yields can

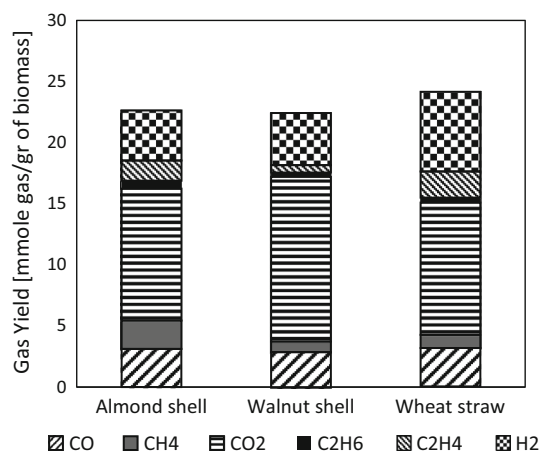


Fig. 2 Gasification yields for different feedstocks (T 440 °C, biomass loading: 0.05 g, water loading: 5 g)

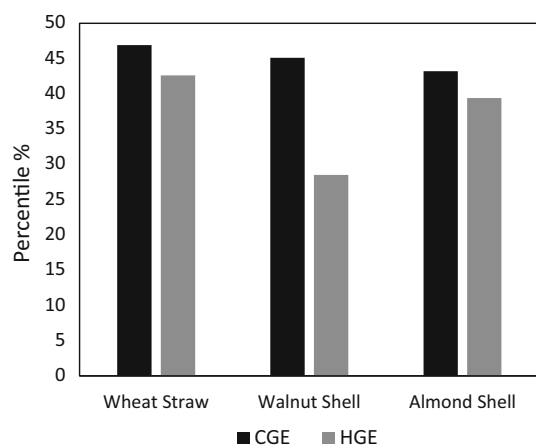


Fig. 3 Hydrogen and carbon gasification efficiencies of feedstocks (T 440 °C, biomass loading: 0.05 g, water loading: 5 g)

show that the structure of walnut shell with more lignin has the lowest total gas yield equal to 22.4 mol/g since the wheat straw has the highest yield with 24.2 mol gas per gram of it. This is because of the higher resistance of lignin during hydrolysis that can postpone the complete gasification. Lignin in the biomass acts as a binding agent that holds cellulose and hemicellulose together, providing firmness to the lingo-cellulosic network. This makes the biomass resistant to various chemicals and enzymes (Kumar et al. 2009). The presence of lignin in biomass makes it difficult to obtain cellulose and hemicellulose to produce fermentable sugars (Reddy et al. 2014). The results in Table 2 show the final composition of the syngas for different feedstocks. SCW gasification process is the result of combination of the series of complex and competing reactions mentioned earlier in this article.

In this study, in addition to comparison between different feedstocks in terms of total gas yield and hydrogen yield per mass unit, the relationship between biomass structure and gas yields was also investigated. There is no certain proved mechanism for supercritical water gasification. However, results indicate that the total gasification yields are approximately related to the total amount of cellulose and hemicellulose in the structure of biomass. This is because of higher solubility of cellulose and hemicellulose compared with lignin, but lignin structure can be dissolved in water in higher temperatures and resident times and specific conditions. Here, wheat straw with higher hydrogen content in its elemental analysis showed the highest hydrogen yield. Therefore, it can be said that the hydrogen content in CHNS analysis has an almost direct relationship with hydrogen gas yield.

Conclusion

The gasification of wheat straw, walnut shell and almond shell in supercritical water media was studied using a batch microreactor with volume 23 mL. These experiments were performed at the temperature 440 °C, 0.05 g biomass loading, and 0.05 g water loading with resident time of 15 min. The hydrogen gas yield of 6.52 mol per gram and the ratio of 27 % in total gas were observed for wheat straw as the highest hydrogen yield among experimented

Table 2 Gas composition and gasification efficiencies for supercritical water gasification of different feedstocks. (T : 440 °C, biomass loading: 0.05 g, water loading: 5 g)

Biomass	Gasification efficiency (%)		Gas composition (mmol gas/g of biomass)					
	HGE	CGE	CO	CH ₄	CO ₂	C ₂ H ₆	C ₂ H ₄	H ₂
Wheat straw	42.6	46.9	3.1933	1.078	10.82	0.41	2.15	6.52
Walnut shell	28.5	45.1	2.86	0.883	13.47	0.362	0.607	4.26
Almond shell	39.4	43.2	3.12	2.31	10.80	0.647	1.65	4.1



feedstocks. Results indicated that wheat straw, walnut shell, and almond shell had the highest hydrogen yield, respectively, and wheat straw, almond shell, and walnut shell showed the highest hydrogen gasification efficiency, respectively. It was also recognized that cellulose and hemicellulose were better gasified than lignin because of their easier hydrolysis and higher solubility in water.

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